

# PATENT SPECIFICATION

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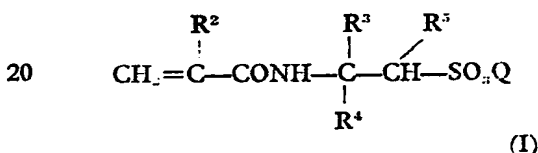


## (54) 2-(β-AMINO-PROPIONAMIDO)-ALKANE SULPHONIC ACID SALTS

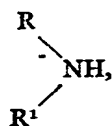
- (71) We, BAYER AKTIENGESSELLSCHAFT, formerly known as Farbenfabriken Bayer Aktiengesellschaft, a body corporate organised under the laws of Germany of 509  
 5 Leverkusen, Germany, do hereby the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—  
 10 This invention relates to 2 - (β - amino - propionamido) - alkane sulphonic acid salts, their preparation and their use as anionic synthesis component in the preparation of emulsifier-free polyurethane dispersions.  
 15 Aminosulphonic acids are used *inter alia* as intermediate products in the production and modification of plastics and in the production of detergents. Diamino sulphonic acids, such as 2,4-diaminobenzene sulphonic acid, and  
 20 their salts are particularly suitable as anionic synthesis component in the preparation of emulsifier-free polyurethane dispersions (Belgian Patent Specification No. 673,432).  
 25 These readily available aromatic diamino sulphonic acids are usually commercial products which, as a rule, are only moderately soluble in the solvents normally used, and furthermore impart to the polyurethanes obtained from them a high sensitivity to light and a marked tendency towards yellowing. Polyurethane dispersions prepared from them are discoloured by light and give coatings, coverings and films which are not fast to light.  
 30 For these reasons, it has hitherto been difficult to produce effectively reproducible light-fast polyurethane dispersions from diaminosulphonic acids which are both economically and physiologically acceptable and which can be obtained commercially in highly pure form.  
 35 Although processes for the production of aliphatic aminosulphonic acids whose salts are suitable for use as anionic synthesis components in the preparation of light-fast polyurethane dispersions, are also known, these processes can only be carried out at appreciable cost in terms of apparatus (e.g. heating hydroxyalkane sulphonic acid salts and amines under pressure), or alternatively they use starting compounds that represent serious health hazards (e.g. reaction of sultones with amines).  
 40 45 50 55 The present invention provides a 2 - (β - aminopropionamido) - alkane sulphonic acid salt of the formula



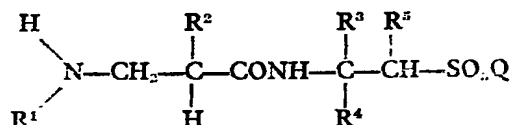
- in which R and R<sup>1</sup> each represents hydrogen or a C<sub>1</sub> to C<sub>18</sub> alkyl or C<sub>3</sub> to C<sub>8</sub>-cycloalkyl group optionally substituted by an amino or alkylamino group and, when R is hydrogen, R<sup>1</sup> may be 4 - (4 - aminocyclohexylmethyl) - cyclohexyl, 3 - (3 - amino - *n* - propoxy) - *n* - propyl or 3 - (3 - amino - *n* - propyl - methylamino) - *n* - propyl;
- 5 R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are the same or different and each represents hydrogen or a C<sub>1</sub> to C<sub>18</sub> alkyl group; and
- 10 Q represents an alkali metal, alkaline earth metal, ammonium or substituted ammonium cation.
- 15 The present invention also relates to a process for the preparation of these 2 - (β - amino - propionamido) - alkane sulphonic acid salts which comprises reacting a compound of the formula



with a compound of the formula



- in which formulae, R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Q have the meanings given above.
- 25 The present invention furthermore relates to a process for preparing an emulsifier-free polyurethane dispersion which comprises reacting a 2 - (β - amino propionamido) - alkane sulphonic acid salt corresponding to the formula
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- in which R<sup>1</sup> represents hydrogen or a C<sub>1</sub> to C<sub>18</sub> or C<sub>3</sub> to C<sub>8</sub> cycloalkyl group, optionally substituted by an amino group or an alkyl-amino group, or R<sup>1</sup> is 4 - (4 - aminocyclohexylmethyl) - cyclohexyl, 3 - (3 - amino - *n* - propoxy) - *n* - propyl or 3 - (3 - amino - *n* - propyl - methylamino) - *n* - propyl, and R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> and Q have the meanings given above, with a preadduct obtained from a polyhydroxyl compound having a molecular weight from 300 to 20,000, a polyisocyanate and optionally a chain extender having active hydrogen atoms and having a molecular weight of up to 300, and mixing the melt obtained by this reaction with water.
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Compounds of formula I can be obtained by acylating amino-alkane sulphonic acid salts with α,β-unsaturated acid chlorides. These starting materials may be prepared with particular advantage from olefins, α,β-unsaturated nitriles and sulphur trioxide (French Patent Specification No. 1,488,814).

The following amines are examples of amines corresponding to the formula RR<sup>1</sup>NH: ammonia, methylamine, ethylamine, *n*-propylamine, *i*-propylamine, *n*-butylamine, *n*-hexylamine, cyclohexylamine, *n*-octylamine, *n*-dodecylamine, *n*-tetradecylamine, *n*-hexadecylamine, *n*-octadecylamine, amine mixtures obtained by reduction from nitro-paraffins, dimethylamine, *N* - methyl - cyclohexylamine, *N* - butyl - cyclohexylamine, *N* - methyl - octadecylamine, 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,4-diaminocyclohexane, 4,4'-diaminodicyclohexylmethane, γ,γ' - diamino - di - *n* - propyl ether, methyl - bis - (3 - aminopropyl) - amine, and bis - (3 - aminopropyl) - amine.

The following compounds are examples of compounds corresponding to formula I used as starting materials in the preparation of the new compounds according to the invention: sodium, potassium or triethylammonium 2 - acrylamido - ethane sulphonate, sodium or potassium 2 - (α - methacrylamido) - ethane sulphonate, sodium 2 - acrylamido - propane sulphonate, sodium 2 - α - methacrylamido - propane sulphonate, sodium 3 - acrylamido - 2 - butane sulphonate, sodium 2 - acrylamido - 1,2,2 - trimethylethane sulphonate, and preferably the sodium, potassium, ammonium, trimethylammonium or triethylammonium salt of 2 - acrylamido - 2,2 - dimethyl ethane sulphonic acid.

The reaction is preferably carried out in a solvent, especially water, stoichiometric quantities of the reagents, or even an excess of amine, preferably being used. The reaction may also be carried out by contacting the starting materials in the absence of solvents, in which case the amine is preferably used in excess.

The reaction temperature is preferably in the range of from room temperature to 150°C., especially from 30 to 100°C.

There is no need to employ elevated pressure during the reaction, although to accelerate the reaction it is best to apply pressure, for example when amines that are gaseous at room temperatures are used.

The molar ratio of amine to compound I is preferably at least 1:1. When a larger ratio is used, any excess amine left on completion of the reaction may be removed for example by distillation, or alternatively it may even be left in the reaction mixture without any detrimental effect in subsequent use.

The novel compounds can be employed as intermediates for the production and modi-

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5 fication of plastics and, in some instances, may also be used as detergents. The 2 - ( $\beta$  - aminopropionamido) - alkane sulphonic acid salts in which R is hydrogen obtained by the process according to the invention, preferably the diamino sulphonates obtainable by the reaction of alkylene diamines with acrylamidoalkane sulphonic acid salts, are particularly suitable for use in the production of 10 ionic, emulsifier-free, polyurethane dispersions.

15 The dispersions prepared from the salts of the  $\beta$ -aminopropionamido alkane sulphonic acids can also be prepared particularly economically and may be used in the production of light-fast colourless films, filaments, coatings, impregnations, bonds and intermediate layers.

20 In the preparation of the aqueous emulsifier-free polyurethane dispersions, a preadduct containing isocyanate groups is best initially prepared from a relatively high molecular weight polyhydroxyl compound with a molecular weight of from 300 to 20,000 and preferably from 600 to 4000, a polyisocyanate and optionally a low molecular weight chain 25 extender containing reactive hydrogen atoms, and is then reacted in organic solution with the salt of the  $\beta$ -aminopropionamido sulphonic acid used in accordance with the invention, optionally in the form of a solution. The resulting, predominantly linear or branched, high molecular weight anionic polyurethanes are converted into the aqueous 30 phase by the addition of water and the organic solvent is simultaneously or subsequently removed, either wholly or in part.

35 It is also possible initially to introduce the salt of the  $\beta$ -aminopropionamido sulphonic acid in aqueous solution and to stir in the preadduct containing isocyanate groups. It is also possible to add all the water together with the  $\beta$ -aminopropionamido acid salt to the preadduct containing isocyanate groups.

40 The relatively high molecular weight polyhydroxyl compounds with a molecular weight of from 300 to 20,000 disclosed in French Patent Specification No. 1,416,564 and in Belgian Patent Specification No. 673,432, polyisocyanates and chain extenders containing reactive hydrogen atoms, are examples of suitable starting components for the preparation of the dispersions.

45 Suitable relatively high molecular weight polyhydroxyl compounds include substantially linear compounds with a molecular weight of from 300 to 20,000, preferably from 600 to 4000; polyesters, polyacetals, polyacetones, polycarbonates, polyethers and polyester amides being preferred. The hydroxyl number of these compounds is generally from 10 to 100 and preferably from 50 to 70. Suitable chain extenders containing reactive hydrogen atoms include glycols, diamines, amino alcohols and water. These compounds may option-

ally be used together with the relatively high molecular weight polyhydroxyl compounds, the low molecular weight compounds generally having molecular weights of up to 300. It is also possible however, to operate in the absence of these low molecular weight compounds. 70

In order to vary the water-repellant properties, the handle and the surface and gloss properties of the impregnations, coatings, coverings and bonds obtained from the end products, it is frequently of advantage to use optionally carbo-functional polysiloxanes with reactive hydroxyl groups and a molecular weight of from 300 to 20,000, preferably from 600 to 4000, optionally in portions, as the relatively high molecular weight polyhydroxyl compounds with a molecular weight of from 300 to 20,000. 75

Carbofunctional polysiloxanes of this kind and their preparation are described for example in French Patent Specification No. 1,291,937, in German Auslegeschrift No. 1,114,632 and in British Patent Nos. 1128642 and 1176490. 80

Suitable polyisocyanates include any aromatic and aliphatic diisocyanates, although aliphatic or cycloaliphatic diisocyanates are particularly preferred for the production of polyurethane compositions which do not discolour under the effect of light. Examples of these diisocyanates include butane - 1,4 - diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, diisocyanato carboxylic acid esters such as 2,6-diisocyanato hexanoic acid ethyl ester, trimethyl hexane diisocyanate, xylene diisocyanate, dicyclohexyl methane diisocyanate, cyclohexane 1,4-diisocyanate, 1-methyl cyclohexane - 2,4 - and 2,6-diisocyanate and mixtures thereof. Examples of aromatic diisocyanates include 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate and 4,4-diisocyanato diphenyl methane. 85

Low-boiling organic solvents such as acetone, tetrahydrofuran, methyl ethyl ketone and tertiary butane diol are preferably used as solvents for the preadduct containing isocyanate groups. It is also possible to use low boiling solvents which are immiscible with water such as benzene and methylene chloride. 90

Low-boiling alcohols, such as methanol and ethanol, or water, optionally containing other organic solvents, may be used as solvents for the salt of the amino sulphonic acid containing amide groups. 95

The preadduct containing isocyanate groups is generally best prepared at elevated temperatures, temperatures of from 110 to 130°C. being used when aliphatic diisocyanates are employed. Temperatures of from 60 to 100°C. are usually sufficient when aromatic diisocyanates are used. To prepare the preadduct, the quantity of polyisocyanate is preferably selected in such a way that all groups 100

reactive with isocyanate groups react. Alternatively, a slight excess of diisocyanate may be used. In general, the ratio of isocyanate groups to the groups reactive with isocyanate groups is no greater than 1.3 to 1.5.

5 After the melt has cooled, the preadduct is taken up in the organic solvent, followed by the addition at 20 to 80°C. of the  $\beta$ -aminopropionamido sulphonic acid salt, 10 optionally in the form of a solution. If excessively high viscosities occur during its preparation, the preadduct may also be prepared in the presence of solvents such as acetone, tetrahydrofuran or methyl ethyl ketone, 15 optionally under pressure.

The proportion of sulphonate groups —SO<sub>3</sub>— in the polyurethane can be from 0.05 to 7% by weight, preferably from 0.5 to 4% by weight. The quantities in which the 20  $\beta$ -aminopropionamido sulphonic acid is used should be selected accordingly. Consequently, the sulphonate group content can be varied within wide limits, although it should not fall below the aforementioned lower limit 25 because otherwise the stability of the dispersions which according to the invention are synthesised in the absence of such auxiliaries as emulsifiers dispersants or swelling agents, is detrimentally affected.

30 For conversion into the aqueous phase, the organic solvent is removed either by distillation or by blowing it out, for example at temperatures of from 30 to 80°C. The solvent is preferably distilled off *in vacuo*.

35 It is possible in this way to obtain aqueous dispersions in the form of low-viscosity to high-viscosity non-sedimenting latices, with an average particle size of from 0.02 to 1.0 and preferably from 0.05 to 0.2, and a solids content of generally from 20 to 60% by weight. 40

If  $\beta$ -aminopropionamido sulphonates which contain only one hydrogen atom linked to the amino nitrogen are used for the preparation 45 of polyurethane dispersions, this preparation may also be carried out in the absence of organic solvents.

In this very considerably preferred method of operation, it is an NCO preadduct which 50 is first produced from the high-molecular-weight polyhydroxyl compound (preferably a polyether or polyester with a molecular weight from 800 to 6000), compounds with at least two isocyanate groups and, if desired, low-molecular-weight glycols, the NCO preadduct 55 having a mean molecular weight of from 2000 to 10,000 and being easily stirrable as a melt. This is achieved by maintaining in the preadduct-forming reaction an NCO/OH ratio of from 1.2 to 3. Preference is given to a ratio of from 1.3 to 2. This preadduct can also be modified with modifier compounds having at least one group reactive 60 towards isocyanates and at least one acylated amino group. Such modifying components 65

having acylated amino groups include, for example, urea, thiourea, sulphamide, methyl urea, ethylene urea, acetoguanamine, glycolic acid amide and 6-aminocaproic acid amide. Further suitable compounds containing acylated amino groups are described in the Belgian Patent Specification No. 730,543. 70

The modifying agents can be added to the reaction mixture before, during, or also after the formation of the NCO prepolymer. 75

Finally, the NCO prepolymer is reacted with the salt of the  $\beta$ -amino-propionamido-sulphonic acid. An isocyanate/amino group ratio of from 0.9 to 1.1 is maintained during the reaction to minimise chain extension and chain branching. 80

The reaction is preferably carried out in the presence of small quantities of water and/or alcohols to ensure good solubility of the sulphonate and miscibility with the prepolymer. 85

For carrying out the reaction, the solution of the amino sulphonate can preferably be stirred into the prepolymer melt. It is advantageous for avoiding side reactions which make the viscosity rise unduly to add the amino sulphonate as quickly as possible in one single portion and to stir it in as quickly as possible. Also after the reaction, the melt should allow easy stirring, should contain 2 to 15% by weight of water and not more than 10% by weight of organic solvent. It preferably contains no organic solvent at all or at most up to 5% by weight of solvent. 90 95 100

The melt obtained by this reaction can then be converted into a polyurethane dispersion by mixing with water, preferably at a temperature from 60 to 120°C. It is advisable to add the water to the melt, with self-dispersion occurring. When operating in the reverse manner, stirring the melt into water, it may be advantageous to use a high-speed agitator or intensive-mixer for better homogenisation. 105 110

Following the formation of a dispersion it is advantageous to carry out a post-condensation of the dispersed polyurethane. Compounds preferably used for this purpose are formaldehyde or compounds that split off formaldehyde or react like formaldehyde, for example urea-, melamine-, or dicyandiamide-precondensates carrying methylol or methylol ether groups. These compounds can conventionally be added already to the reaction mixture before it is mixed with water, provided that this does not cause any further increase in viscosity. They may, however, also be added together with water, or part of the quantity of water required for dispersion, or also following the formation of the dispersion. It is also possible to add polyisocyanates in addition to, or instead of, formaldehyde or formaldehyde derivatives. 115 120 125

For carrying out the post-condensation in 130

dispersion, the latter is heated for a short period of time at a higher temperature, for example for one minute at 130°C. or for two hours at 80°C., and/or adjusted to a pH value below 7. The post-condensation may, of course, also take place on the substrate, after the dispersion has dried.

It is thus possible to obtain aqueous dispersions in the form of non-sedimenting low-to high-viscosity latices with a mean particle size of from 0.02 to 1.0, preferably from 0.05 to 0.2, and a solids content of, as a rule, 20 to 60% by weight.

The dispersions usually dry at room temperature or elevated temperatures to form dimensionally stable films and coatings. Relatively high temperatures are preferably used to dry the dispersions. The dispersions obtained according to the invention may also be subsequently crosslinked, for example by polyfunctional compounds with a crosslinking effect such as formaldehyde, compounds which react as formaldehyde such as hexamethylol melamine or carbamide resins, or by phenolic resins, masked polyisocyanates or polyepoxides. In this embodiment, cross-linked coatings, impregnations and adhesives layers are obtained.

The dispersions according to the invention are primarily used as coatings and impregnations for a variety of substrates such as paper, cardboard, textiles, leather, webbing, wood and metals, as adhesion promoters, binders and adhesives, and in the production of filaments, films and foils. The mouldings, coatings and impregnations obtained from the dispersions are distinguished by their outstanding resistance both to wear and to oils, and, compared with the products prepared in accordance with Belgian Patent Specification No. 673,432 using 2,4-diamino benzene sulphonic acid for example, they are colourless and fast to light, both desirable properties.

The dispersions may be blended with anionic polymer or copolymer dispersions, for example of vinyl chloride, ethylene, styrene, butadiene, vinylidene chloride, vinyl acetate, acrylate and acrylonitrile. Fillers, plasticisers, pigments, carbon black, aluminium, clay and tar dispersions may also be worked into the dispersions.

#### Example 1

A solution of 207 g. of 2 - acrylamido - 2,2 - dimethyl ethane sulphonic acid and 500 ml. of water is neutralised with 40 g. of sodium hydroxide dissolved in 100 ml. of water. 120 g. of ethylene diamine are added dropwise with stirring at room temperature, producing a rise in temperature. The reaction mixture is kept at 60°C. for 4 hours following the addition. The excess ethylene diamine is then removed by steam distillation. The resulting solution may be directly used as a starting material in the preparation of

anionic salt urethane dispersions. 290 g. of sodium 2 - [ $\beta$  - ( $\omega$  - aminoethyl amino) propionamido] - 2,2 - dimethyl ethane sulphonate, are obtained by concentrating the solution through evaporation.

#### Example 2

A solution of 207 g. of 2 - acrylamido - 2,2 - dimethyl ethane sulphonic acid in 500 ml. of water is neutralised with 280 g. of 20% by weight potassium hydroxide solution. 116 g. of hexamethylene diamine are added with stirring at room temperature. The reaction mixture is then kept at 50°C. for 6 hours, after which the water is removed by heating *in vacuo*. A solid consisting primarily of potassium 2 - [ $\beta$  - ( $\omega$  - aminohexyl amino) propionamido] - 2,2 - dimethyl ethane sulphonate is obtained in a yield of 358 g.

#### Example 3

132 g. of  $\omega,\omega'$ -diaminodipropyl ether are added dropwise at 20°C. to 115 g. of sodium 2 - acrylamido - 2,2 - dimethyl ethane sulphonate dissolved in 500 ml. of water. The mixture is then stirred for 2 hours at 50°C. Excess amine is then distilled off with steam. After the solution has been concentrated through evaporation, the crude reaction product of  $\omega,\omega'$ -diaminodipropyl ether and sodium 2 - acrylamido - 2,2 - dimethyl ethane sulphonate is obtained in a yield of 190 g.

#### Example 4

229 g. of sodium 2 - acrylamido - 2,2 - dimethyl ethane sulphonate are dissolved in 1 litre of concentrated aqueous ammonia solution, and the resulting solution is kept at 35°C. for a period of 9 hours. After concentration through evaporation, sodium 2 - [ $\beta$  - aminopropionamido] - 2,2 - dimethyl ethane sulphonate is obtained in a yield of 245 g.

#### Example 5

99 g. of cyclohexylamine are added dropwise at 50°C. to a solution of 229 g. of sodium 2 - acrylamido - 2,2 - dimethyl ethane sulphonate in 500 ml. of water. The solution is stirred at this temperature for a period of 4 hours after which the solvent is removed by evaporation *in vacuo*. Sodium 2 - [ $\beta$  - cyclohexylamino propionamido] - 2,2 - dimethyl ethane sulphonate is obtained in a yield of 327 g.

#### Example 6

283 g. of methyl-stearylamine are added to a solution of 229 g. of sodium 2 - acrylamido - 2,2 - dimethyl ethane sulphonate in 1000 ml. of water. The mixture is vigorously stirred for 7 hours at 85°C., as a result of which the amine is dissolved. The solution is concentrated by evaporation in a spray

dryer. Sodium 2 - [ $\beta$  - methyl - stearyl-amino) - propionamido] - 2,2 - dimethyl ethane sulphonate is obtained in a yield of 510 g.

#### 5 Example 7

250 g. of an adipic acid-ethylene glycol polyester (OH number 56) are dehydrated for 30 minutes at 120°C. and then reacted for 2 hours with 38 g. of 1,6-hexane diisocyanate at a temperature of 120°C. This preadduct containing isocyanate groups is cooled to 55°C. and taken up with 700 ml. of acetone. 31.4 g. of sodium 2 - [ $\beta$  - ( $\beta$  - aminoethylamino) - propionamido] - 2,2 - dimethyl ethane sulphonate solution (prepared as in Example 1) in 60 ml. of water are then added to this acetone preadduct solution with vigorous stirring. 450 ml. of water are then stirred in. The batch is stirred until the streaks which initially appear have disappeared and the mixture has become homogeneous. The acetone is distilled off in a water-jet vacuum at 55°C. The dispersion obtained has a solids content of 42.5% by weight and dries at room temperature to form clear colourless films which have outstanding elasticity and tensile strength.

#### 30 Example 8

425 g. of an adipic acid - 1,6 - hexane diol-neopentyl glycol polyester (molar ratio 30:22:12, OH number 67) are dehydrated for 30 minutes at 120°C. and then reacted for 2 hours at 120°C. with 76 g of 1,6-hexane diisocyanate. The resulting preadduct containing isocyanate groups is cooled and taken up in 1500 ml. of acetone. 29.2 g of potassium 2 - [ $\beta$  - ( $\omega$  - aminohexylamino) - propionamido] - 2,2 - dimethyl ethane sulphonate (prepared in accordance with Example 2) in 60 ml. of water are introduced

into this preadduct solution. After brief stirring, 700 ml. of water are added and the acetone is distilled off *in vacuo*. This dispersion - obtained has a solids content of 43.5% by weight and dries to form clear colourless films of outstanding tensile strength. 45

#### Example 9

250 g. of an adipic acid-ethylene glycol polyester (OH number 56) are dehydrated for 30 minutes at 120°C. and then reacted for 2 hours at 120°C. with 41 g. of methyl cyclohexane - diisocyanate isomer mixture (isomer ratio 2,4-diisocyanate: 2,6-diisocyanate 80:20). The resulting prepolymer melt is cooled to 55°C. and taken up in 700 ml. of acetone. 29.95 g. of sodium 2 - [ $\beta$  - ( $\beta$  - aminoethyl amino) - propionamido - 2,2 - dimethyl ethane sulphonate solution (prepared in accordance with Example 1) in 70 ml. of water are added to the acetone solution with vigorous stirring. 50 ml. of water are then stirred in and the acetone is distilled off in a water-jet vacuum at 55°C. The resulting dispersion, having a solids content of 38.5% by weight, dries to form flat, firm coatings. 50 55 60 65

#### Example 10

The procedure is as in Example 9, except that 250 g. of polypropylene glycol ether (OH number 56) are used instead of the polyester, and the prepolymerisation reaction is carried out at 130°C. instead of at 120°C. A stable dispersion with a solids content of 39% by weight is obtained which dries to form a soft slightly tacky film. 70 75

#### Example 11

314.8 g. of a hydroxyl-group-containing carbofunctional polysiloxane of the average formula 80



containing 2.7% by weight of OH are dehydrated at 120°C. and then mixed at 90°C. with 81 g. of 1,6-hexane diisocyanate, and reacted for 2 hours at 100°C. After cooling to 50°C., the liquid reaction mixture is taken up in 1000 ml. of acetone, followed by the addition of 37.2 g. of potassium 2 - [ $\beta$  - ( $\omega$  - aminohexyl amino)propionamido] - 2,2 - dimethyl ethane sulphonate (prepared in accordance with Example 2) in 80 ml. of water. After brief stirring, 650 ml. of water are stirred in and the acetone is distilled off *in vacuo*. The dispersion obtained, which has a solids content of 40.5% by weight, dries to form a wax-like film. 85 90 95

#### Example 12

400 g. (0.169 mole) of an adipic acid/diethylene glycol polyester and 41 g. of 1,6-

hexamethylene diisocyanate are stirred for two hours at 120 to 130°C. The resulting prepolymer melt is cooled to 80°C. and stirred into a 50% by weight aqueous solution of sodium 2 - ( $\beta$  - cyclohexyl - amino - propionamido) - 2,2 - dimethylethane - sulphonate within two minutes. An increase in viscosity occurs within four minutes, but the water-containing melt can still be stirred easily. 1,050 cm<sup>3</sup> of water at 90°C. are stirred in within twenty minutes, a viscous latex being formed. After the latex has cooled down, 100 g. of 30% by weight aqueous formaldehyde solution are added. 100 105 110

The latex can be adjusted to a pH value of from 3 to 4 by means of phosphoric acid or tartaric acid and yields, after drying and subsequent short-term heating at 120°C., elastic and soft films of good firmness. 115

## Example 13

400 g. (0.169 mole) of an adipic acid/diethylene glycol polyester and 20 cm<sup>3</sup> of a 10% by weight solution of sulphur dioxide in dioxane are stirred at 120°C. *in vacuo* for thirty minutes, with dehydration and dealkalisation occurring. 35.6 g. of 1,6-hexamethylene diisocyanate are added and the resulting mixture is subsequently stirred for two hours at 124 to 135°C. and cooled to 98°C. A solution of 36 g of sodium 2 - (β - cyclohexylaminopropionamido) - 2,2 - dimethylethane - sulphonate in 40 g of 50% by weight isopropanol is then stirred into the mixture. The resulting viscous solution is then stirred with 1050 cm<sup>3</sup> of water within thirty minutes at 77°C. and 30 g. of 30% by weight aqueous formaldehyde solution at 76°C. A viscous and stable latex is obtained in a yield of 1428 g.

## Example 14

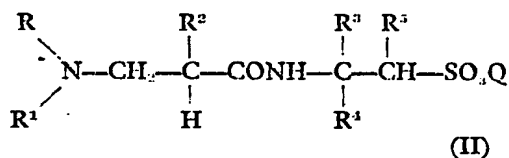
The procedure is as in Example 13, but using 280 g. of a phthalic acid/adipic acid/ethylene glycol polyester having a molecular weight of 1750. A viscous, white latex is obtained.

## Example 15

The procedure is as in Example 13, but using 29 g. of sodium 2 - (β - methylamino - propionamido) - 2,2 - dimethylethane - sulphonate. 1500 cm<sup>3</sup> of water are stirred into the mixture to form a dispersion. A viscous and stable polyurethane latex is obtained which, after acidification with phosphoric acid to pH of 3 and subsequent heating at 120°C., dries to form a soft film resistant to tensile stress.

## WHAT WE CLAIM IS:—

1. A 2 - (β - aminopropionamido) - alkane sulphonic acid salt of the formula



in which R and R<sup>1</sup> each represents hydrogen or a C<sub>1</sub> to C<sub>18</sub> alkyl or C<sub>1</sub> to C<sub>8</sub>-cycloalkyl group optionally substituted by an amino or alkylamino group and, when R is hydrogen, R<sup>1</sup> may be 4 - (4 - aminocyclohexylmethyl) - cyclohexyl, 3 - (3 - amino - *n* - propoxy) - *n* - propyl or 3 - (3 - amino - *n* - propyl - methylamino) - *n* - propyl;  
R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are the same or different and each represents hydrogen or a C<sub>1</sub> to C<sub>4</sub> alkyl group; and  
Q represents an alkali metal, alkaline earth metal, ammonium or substituted ammonium cation.

2. Sodium 2[β - (ω - aminoethylamino) propionamido] - 2,2 - dimethyl ethane sulphonate.

3. Potassium 2 - [β - (ω - aminoethylamino) propionamido] 2,2 - dimethyl ethane sulphonate.

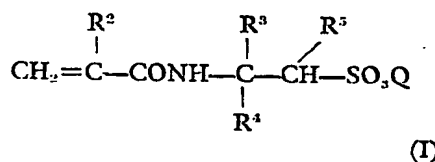
4. The reaction product of ω,ω' - diamino - dipropyl ether and sodium 2 - acrylamido - 2,2 - dimethyl ethane sulphonate.

5. Sodium 2 - [β - aminopropionamido] - 2,2 - dimethyl ethane sulphonate.

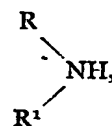
6. Sodium 2 - [β - cyclohexylamino - propionamido] - 2,2 - dimethyl ethane sulphonate.

7. Sodium 2 - [β - (methyl - stearyl - amino) - propionamido] - 2,2 - dimethyl ethane sulphonate.

8. A process for preparing a 2 - (β - aminopropionamido) - alkane sulphonic acid salt according to claim 1 which comprises reacting a compound of the formula



with a compound of the formula



in which formulae R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Q have the meanings given in claim 1.

9. A process as claimed in claim 8 wherein reaction is carried out in a solvent.

10. A process as claimed in claim 9 wherein the solvent is water.

11. A process as claimed in any of claims 8 to 10 wherein reaction is carried out at a temperature in the range from room temperature to 150°C.

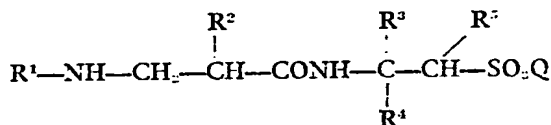
12. A process as claimed in claim 11 wherein the temperature is from 30 to 100°C.

13. A process as claimed in claim 8 substantially as hereinbefore described.

14. A process as claimed in claim 8 substantially as described with reference to any of Examples 1 to 6.

15. A 2 - (β - aminopropionamido) - alkane sulphonic acid salt when prepared by a process as claimed in any of claims 8 to 14.

16. A process for preparing an emulsifier-free polyurethane dispersion which comprises reacting a 2 - (β - aminopropionamido) - alkane sulphonic acid salt of the formula



- wherein  $R^1$  represents hydrogen or a  $C_1$  to  $C_4$  alkyl or  $C_2$  to  $C_4$  cycloalkyl group optionally substituted by an amino or alkylamino group, or  $R^1$  is 4 - (4 - aminocyclohexylmethyl) - cyclohexyl, 3 - (3 - amino -  $n$  - propoxy) -  $n$  propyl or 3 - (3 - amino -  $n$  - propyl - methylamino) -  $n$  - propyl, and  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $Q$  have the meanings given in claim 1, with a preadduct obtained from a polyhydroxyl compound having a molecular weight from 300 to 20,000, a polyisocyanate and optionally a chain extender containing active hydrogen atoms and having a molecular weight of up to 300, and mixing the melt obtained by this reaction with water.
17. A process as claimed in claim 14 wherein the polyhydroxyl compound has a molecular weight of from 600 to 4,000.
18. A process as claimed in claim 16 or 17, wherein the polyhydroxyl compound has a hydroxyl number of from 10 to 100.
19. A process as claimed in claim 18 wherein the polyhydroxyl compound has a hydroxyl number of from 50 to 70.
20. A process as claimed in any of claims 16 to 19 wherein the polyhydroxyl compound is an optionally carbofunctional polysiloxane having reactive hydroxyl groups.
21. A process as claimed in any of claims 16 to 19 wherein the polyhydroxyl compound is a polyester, polyacetal, polyacetone, polycarbonate, polyether or polyesteramide having hydroxyl groups.
22. A process as claimed in any of claims 16 to 21, wherein the chain extender is a glycol, diamine, or amino-alcohol or water.
23. A process as claimed in any of claims 16 to 22 wherein reaction is carried out in solution in an organic solvent, and the product is mixed with water and the organic solvent is wholly or partially removed.
24. A process as claimed in any of claims 16 to 23 which is carried out in the presence of water.
25. A process as claimed in any of claims 16 to 24 wherein the preadduct is modified with a modifier compound having at least one group reactive towards isocyanates and at least one acylated amino group.
26. A process as claimed in claim 25 wherein the modifier compound is urea, thiourea, sulphamide, methylurea, ethylene urea, acetoguanamine, glycolic acid amide or 6-aminocaproic acid amide.
27. A process as claimed in any of claims 16 to 26 wherein the isocyanate/amino group ratio during the reaction is from 0.9 to 1.1.
28. A process as claimed in any of claims 16 to 27 wherein the polyurethane obtained is post-condensed with formaldehyde, a compound that splits off formaldehyde or reacts like formaldehyde, and/or a polyisocyanate.
29. A process as claimed in claim 16 substantially as hereinbefore described.
30. A process as claimed in claim 16 substantially as described with reference to any of Examples 7 to 11.
31. A process as claimed in claim 16 substantially as described with reference to any of Examples 12 to 15.
32. Emulsifier-free polyurethane dispersions when prepared by a process as claimed in any of claims 16 to 31.

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